THE SILICATE MATERIAL IN COMETS

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Abstract. Silicates in comets appear to be a mix of high–temperature crystalline enstatite and forsterite plus glassy or amorphous grains that formed at lower temperatures. The mineral identifications from the 10 and 20 μm cometary spectra are consistent with the composition of anhydrous chondritic aggregate IDPs. The origin of the cometary silicates remains puzzling. While the evidence from the IDPs points to a pre-solar origin of both crystalline and glassy components, the signatures of crystalline silicates appear in the spectra of young stellar objects only at a late evolutionary stage, when comets are the likely source of the dust.

1. Introduction

Silicates comprise a major part of the non-volatile material in comets. Silicate grains are also abundant in interstellar clouds and in the envelopes of oxygen-rich evolved stars. At present, it is not clear where the cometary silicates originated. Comets formed in regions of the solar nebula that were cold enough for interstellar silicate grains to have been incorporated without thermal alteration. However, their prior history in the solar nebula is not known. Were they shock heated during infall to the circumsolar disk? Were they altered by collisions? Was there extensive mixing between warm and cold regions of the solar nebula? Did small grains experience heating events similar to those that produced chondrules?

Up to the present, our knowledge of cometary silicates comes primarily from two sources: remote observations of infrared spectral features and in situ sampling of the dust composition during the Halley flybys. Yet, there is another very important means for learning about cometary dust. Particles released from comets are among the interplanetary dust particles (IDPs) swept up by the Earth and retrieved for laboratory analysis. If we can identify which IDPs are from comets, then we have a powerful means to study the structure, mineralogy, and history of the cometary silicates.

Comet Hale-Bopp has brought us a big step closer to deducing the mineralogy of cometary silicates and their relation to IDPs. In this paper, I summarize what is known about cometary silicates and discuss the link between cometary silicates, the chondritic aggregate interplanetary dust particles, and interstellar grains.

2 M.S. HANNER

2. Silicate Spectral Features in Comets

Silicate particles produce a spectral feature near 10 μm due to stretching vibrations in Si–O bonds. Additional bending mode vibrations occur between 16 and 35 μm. The wavelengths and shapes of these features are diagnostic of the mineral composition. The 10 μm feature lies within the 8–13 μm atmospheric "window" allowing ground–based observations. Although 20 μm observations can also be made from the ground, the full 16–35 μm region is best observed from above the atmosphere.

A broad 10 μm emission feature is visible in filter photometry of many new and long–period comets, beginning with the first infrared observations of comet Ikeya–Seki in 1965 (Becklin and Westphal 1966, Ney 1982, Gehrz and Ney 1992). The feature is strongest in active comets which have a strong scattered light continuum at visible wavelengths.

Low–resolution 8–13 μm spectra with good signal/noise have been acquired for about a dozen comets. (See Hanner et al. 1994a for a review.) Six of the comets display a strong structured emission feature. These are long–period comets Bradfield (1987 XXIX = C/1987 P1) (Hanner et al. 1994a), Levy (1990 XX = C/1990 K1) (Lynch et al. 1992), Hyakutake, Hale–Bopp (C/1995 O1), (Hayward and Hanner 1997; Hanner et al. 1998b; Wooden et al. 1999), new comet Mueller (1994 I = C/1993 A1) (Hanner et al. 1994b) and P/Halley (Bregman et al. 1987; Campins and Ryan 1989).

By far the strongest emission feature is seen in comet Hale–Bopp, (Fig. 1). One sees 3 peaks, at 9.2, 10.0, and 11.2 μm and minor features at 11.9 and 10.5 μm. These peaks appear consistently in spectra taken with three different instruments under a wide range of observing conditions (Hanner et al. 1998b). The spectral shape is similar in comet P/Halley (Fig. 1) and the other comets cited above. However, the lower signal/noise in previous spectra meant that only the 11.2 μm peak was confidently identified (Bregman et al. 1987, Campins and Ryan 1989, Hanner et al. 1994a).

Transmission spectra of various amorphous and crystalline silicates have been measured in the laboratory (e.g. Koike et al. 1993, Dorschner et al. 1995, Colangeli et al. 1995, Day 1979). Transmission spectra of the silicates in chondritic aggregate IDPs were reported by Sandford and Walker (1985). Direct emission spectra of both amorphous and crystalline pyroxene (enstatite) and olivine (forsterite) were obtained by Stephens and Russell (1979). Except for scattering in the wings, Stephens and Russell did not find any systematic differences between the transmission and emission spectra of their samples. Both transmission and emission spectra will be used here to interpret the comet spectra.

The 11.2 μm peak and the 11.9 μm shoulder are attributed to crystalline olivine, based on the good spectral match with the measured spectral emissivity of Mg–rich crystalline olivine (Stephens and Russell 1979; Koike et

al. 1993). The 9.2 μm feature (Fig. 2) corresponds to amorphous, Mg–rich pyroxene (Stephens and Russell 1979; Dorschner et al. 1995). The broad maximum at 9.8–10.0 μm is similar to that seen in many interstellar sources and is most likely produced by amorphous or glassy olivine particles. The overall width of the cometary spectral feature, the relatively flat top from 10–11 μm, and the structure near 10.5 μm can best be fit with crystalline pyroxenes. Crystalline pyroxenes have considerable variety in their spectral shapes. The orthorhombic orthoenstatite measured by Stephens and Russell has a narrow feature sharply peaked at 9.90 μm. While orthoenstatite and clinoenstatite are found together, clinoenstatite is the more common form in chondritic aggregate IDPs (Bradley et al. 1992). These pyroxene-rich IDPs have a broader spectral feature with major peaks in the 10-11 μm spectral region (Sandford and Walker 1985).

An example of a composite spectrum composed of these 4 components is compared with the Hale–Bopp spectrum in Fig. 3 (Hanner et al. 1998b). The transmission spectrum of "Key" IDP (Sandford and Walker 1985) was adopted for the crystalline pyroxene; the other emissivities are from Stephens and Russell (1979). Other fits using similar components are presented in Wooden et al. (1999).

It is not possible to quantify the relative abundances of these different silicate components for several reasons. 1) The laboratory measurements of spectral transmission and emissivity are only relative and do not give the quantitative mass absorption coefficients. 2) The strength of the feature depends on particle size. 3) Mie theory, in wide use for modeling the scattering and emission from small spherical particles, is not applicable for the crystalline silicates even when measured optical constants are available because of the strong dependence on particle shape near a resonance in the optical constants (Bohren and Huffman 1983). 4) Thermal emission from a particle depends upon its temperature. The temperature is controlled by the balance between absorption of solar radiation and infrared emission and will vary with grain size, Mg/Fe ratio, and any admixture of dark material (Hanner et al. 1998b; Wooden et al. 1999). If the temperatures of the various silicate components are comparable, then the stronger mass absorption coefficient of forsterite implies it constitutes not more than 10% –20% of the silicates.

Silicates also have bending mode vibrations at 16–24 μm; the central wavelength depends on the mineral structure. A remarkable 16–45 μm spectrum of comet Hale–Bopp at $r = 2.9$ AU was acquired with the SWS spectrometer on the Infrared Space Observatory (Crovisier et al. 1997). Five peaks are clearly visible, corresponding in every case to laboratory spectra of Mg–rich olivine (Koike et al. 1993). Airborne spectra of comet P/Halley at $r = 1.3$ AU (the only other 16–30 μm spectra of a comet) show only weak olivine features at 28.4 and 23.8 μm (Herter et al. 1987).

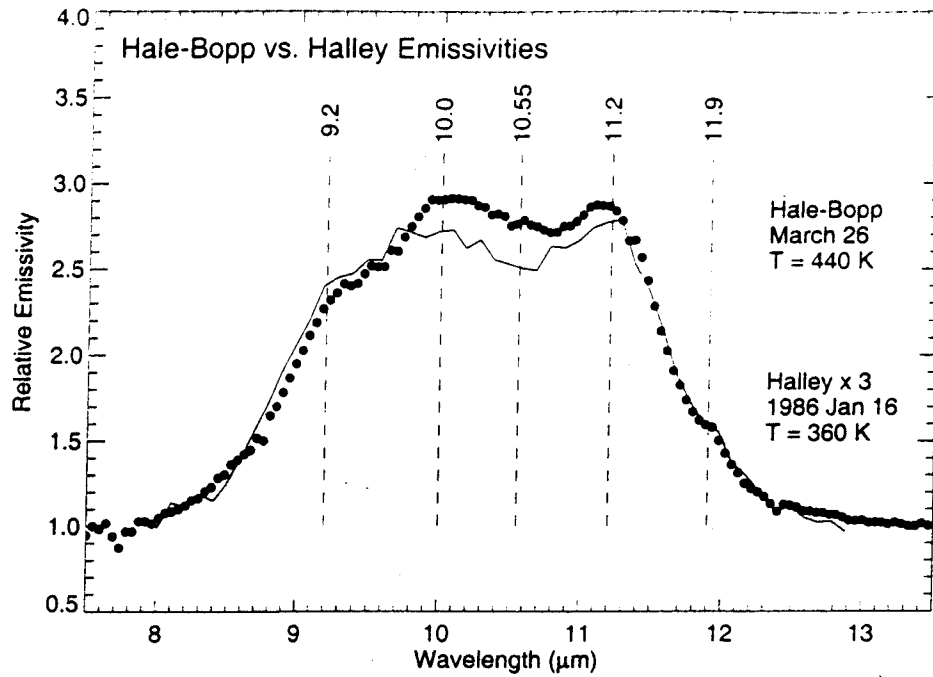*Figure 1.* Silicate feature in Hale-Bopp (points) at *r* = 0.92 AU (Hanner et al. 1998b) and Halley (line) at *r* = 0.79 AU (Campins and Ryan 1989). In each case, the total flux has been divided by a blackbody for the indicated temperature fit at 7.8-8.0 μm and 12.8-13.5 μm. The spectral shapes are remarkably similar, with a peak at 11.2 μm, broad maximum near 10 μm, shoulder near 9.2 μm, and possible structure near 10.5 μm. The inflection at 11.9 μm is also real.
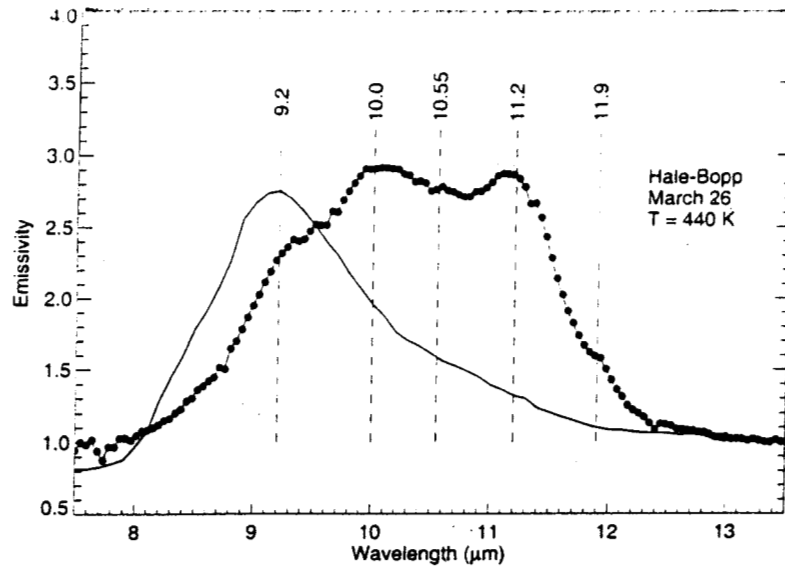
Figure 2. Emissivity of amorphous enstatite (Stephens and Russell 1979) compared with the spectrum of Hale-Bopp (Hanner et al. 1998b). The peak position at 9.2 μm matches the shoulder in the comet spectrum.
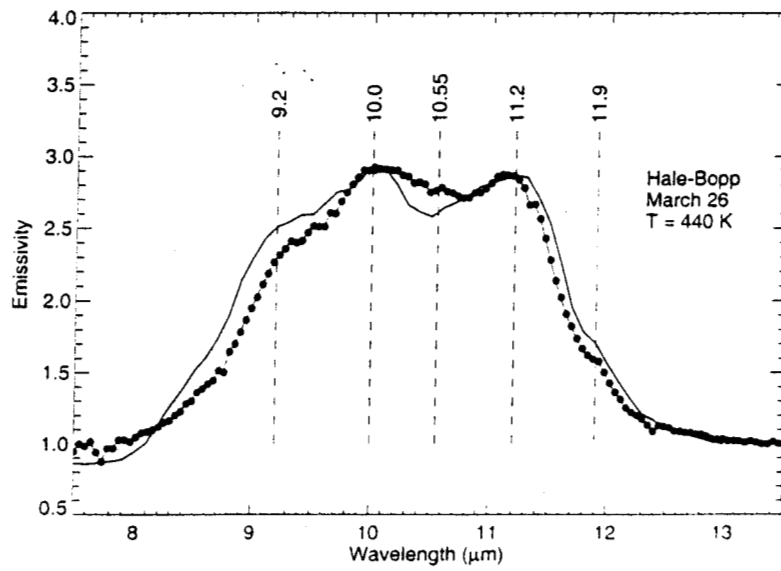

Figure 3. Composite spectral fit to Hale-Bopp (Hanner et al. 1998b) based on measured emissivities of amorphous enstatite, amorphous olivine, and forsterite (Stephens and Russell 1979) and "Key" pyroxene IDP (Sandford and Walker 1985).

The inference from the spectra that the cometary silicates are Mg-rich is consistent with in situ results from comet Halley. The Vega and Giotto space probes carried a time of flight mass spectrometer to measure the elemental composition of impacting dust particles (Kissel et al. 1986; Jessberger et al. 1988 and this volume). Two main grain types were recognized, silicate, or rock, particles dominated by ions of the major rock-forming elements Mg, Si, Ca, Fe, and CHON particles, enriched in the lighter elements, H,C, N,O. The rock particles displayed a wide range of Mg/Fe; in general, the silicates appeared to be depleted in iron, with some of the iron occurring as FeO.

The spectra of four other new comets discussed in Hanner et al. (1994a) are puzzling; each has a unique, and not understood, spectrum. For example, the feature is extremely broad in Wilson (1987 VII), suggesting a very amorphous silicate material. We may be witnessing the effect of cosmic ray damage to the outermost layer of the nucleus over the lifetime of the Oort Cloud.

Short-period comets usually exhibit either a broad, weak 10 μm emission feature above a black-body continuum, such as 4P/Faye and 19P/Borrelly (Hanner et al. 1996) or no feature at all, such as 23P/Brorsen–Metcalf (Lynch et al. 1992). These comets may lack a silicate feature because there is a deficiency of small grains rather than a lack of silicate material. However, a weak 11.2 μm peak was detected in the ISOCAM CVF spectrum of 103P/Hartley 2, the first time crystalline silicates have been observed in a short-period comet (Crovisier et al. 1999).

3. Interplanetary Dust Particles from Comets

The submicron grain size, high Mg/Fe ratio, and mix of crystalline and glassy (or amorphous) olivine and pyroxenes have no counterpart in any meteoritic material, with the exception of the anhydrous chondritic aggregate interplanetary dust particles (IDPs). These are fine-grained heterogeneous aggregates having chondritic abundances of the major rock– forming elements; they comprise a major fraction of the IDPs captured in the stratosphere. Typical grain sizes within the aggregates are 0.1–0.5 μm. These aggregate IDPs are thought to originate from comets, based on their porous structure, high carbon content, and relatively high atmospheric entry velocities. The match between the mineral identifications in the Hale–Bopp spectra and the silicates seen in the IDPs strengthens the link between comets and anhydrous chondritic aggregate IDPs.

The chondritic aggregate IDPs divide into 3 classes based on their infrared spectra, dominated respectively by pyroxenes, olivine, and layer lattice silicates (Sandford and Walker 1985), although a given IDP may contain some grains of all 3 types. The IDPs dominated by layer lattice silicates have low-

er atmospheric entry velocities and less porous structure, consistent with an asteroidal origin. The pyroxene and olivine rich IDPs of probable cometary origin are unequilibrated mixtures of high and low temperature constituents, containing small glassy or microcrystalline silicate grains and larger single crystals of enstatite or olivine (0.5–5 μm in size) along with carbonaceous material and FeS grains (Bradley et al. 1992).

Some of the crystalline silicate grains are enstatite whiskers, ribbons, and platelets with growth patterns that indicate direct vapor phase condensation from a hot gas (Bradley et al. 1983). Such growth patterns would not have formed if the crystals were annealed from glassy silicate grains. The pure Mg crystalline silicates forsterite and enstatite are predicted from thermo-dynamic models to be the first to condense in a hot gas at 1200–1400 K. A likely origin for the enstatite and olivine crystals is in the circumstellar outflows of oxygen–rich evolved stars.

The most intriguing component of the anhydrous chondritic aggregate IDPs are the GEMS, 0.1–0.5 μm glassy Mg silicate grains with embedded nanometer sized FeNi and Fe sulfide crystals (Bradley 1994). The GEMS bear evidence of exposure to large doses of ionizing radiation, such as sputtered rims, Mg/Si/O gradients, and formation of reduced FeNi metal. This radiation exposure must have pre-dated their incorporation into comets, since the inferred dosage greatly exceeds their recent exposure in interplanetary space after release from the parent body. Some GEMS contain relict mineral grains with deeply ion-etched surfaces. GEMS constitute the major component of non-crystalline silicate grains in these IDPs.

Bradley (1994) argues for an interstellar origin of the GEMS, citing their high irradiation dosage, the relict microcrystals, and similarity to the inferred properties of interstellar silicates. The FeNi inclusions are sufficient for the superparamagnetic grain alignment of interstellar grains (Jones and Spitzer 1967; Goodman and Whittet 1995). Interstellar silicates, such as the Trapezium, show a smooth asymmetric silicate feature with a single 9.8 μm maximum consistent with glassy or amorphous olivine. Bradley et al. (1999) report that the infrared spectra of individual GEMS closely resemble the Trapezium spectrum.

4. Origin of the Cometary Silicates

As we have discussed, comets contain a mixture of silicates, both amorphous and crystalline, that do not necessarily share a common origin. Comets formed in regions of the solar nebula where the temperature was too low to sublimate refractory interstellar grains. Boss (1994, 1998) predicts that the temperature at $r \geq 5$ AU was ≤ 160 K. The high CO:H_2O ratio in comets implies that even interstellar ices may have survived. Thus, it is possible

that *all* cometary silicates are of pre-solar origin. In the following paragraphs, evidence regarding the origin of amorphous and crystalline silicates is briefly discussed.

The GEMS described in Section 3 appear to constitute the major fraction of the non-crystalline silicates in cometary IDPs, and the evidence is quite strong that these are interstellar grains. Absorption spectra of GEMS show a 9.8 μm maximum typical of glassy olivine, although a 9.3 μm shoulder indicative of pyroxene is present in some samples (Bradley et al. 1999), and this is consistent with the cometary spectra. It is likely, then, that the bulk of the amorphous cometary silicates are of interstellar origin.

The crystalline silicates are more controversial. Crystalline grains can form by direct condensation from the vapor phase at T = 1200–1400 K with very slow cooling or by annealing (heating) of amorphous silicate particles. While the enstatite whiskers and ribbons must have condensed from a hot gas, other crystalline grains in IDPs have no distinctive structure to distinguish between annealing or direct condensation. Direct condensation provides a natural explanation for Mg-rich silicates, because forsterite and enstatite are the first to condense in a hot gas and only react with Fe at lower temperatures. It is not so easy to explain why annealed grains should convert to pure forsterite and enstatite unless the glassy precursors had the correct stochiometry. Koike and Tsuchiyama (1992) created crystalline olivine by heating glassy Mg-silicate particles for 105 hours at 875 K. The annealing rate drops by orders of magnitude at lower temperatures (Hallenbeck et al. 1998).

Heating is insufficient to anneal the silicates in the coma or on the nucleus. The 11.2 μm peak is observed at the same strength relative to the 10 μm maximum in both new and evolved comets over a wide range in heliocentric distance, from 4.6 AU (Hale-Bopp; Crovisier et al. 1996), where the blackbody temperature is only 130 K, to 0.79 AU (P/Halley; Campins and Ryan 1989). Nor does the 11.2 μm peak increase with time as the grains move outward through the coma. Thus, the crystalline grains must have been present in the solar nebula where the comets accreted.

The crystalline grains could not have been created by the short-term heating events that produced the chondrules. These millimeter sized components of chondritic meteorites required heating to about 1800 K followed by rapid cooling of order 1000 K/hr (Hewins 1988), too rapid to allow crystal growth.

Direct grain condensation or annealing could have occurred in the hot inner solar nebula. Disk midplane temperatures $\geq$ 1000 K were reached inside about 1 AU, depending on mass infall rate (Chick and Cassen 1997; Boss 1998). Accretion shock heating of silicates was significant only at small $r \leq 1$ AU (Chick and Cassen 1997). Transport of micron-sized grains from 1 AU to 10–30 AU is problematical, however. Cuzzi et al (1993) have com-

puted that small grains entrained in the outflowing gas near the midplane of the solar nebula could drift radially outward roughly 2–5 AU before accretion onto larger particles. Grain growth by accretion was a relatively rapid process, limiting the time available for radial diffusion. If sufficient mixing did take place to transport crystalline silicates to the comet formation zone, then other thermally processed components, such as refractory organics, could also have been transported.

Could the crystalline silicates have a pre-solar origin? Thanks to ISO, we now have a better picture of the distribution of crystalline silicates in astronomical sources. Forsterite is detected in oxygen-rich outflows of some evolved stars (Waters et al. 1996). It is also seen in debris disks around young main-sequence objects such as β Pictoris (Knacke et al. 1993) and in late-stage Herbig Ae/Be stars that are the precursors of β Pictoris systems (Waelkens et al. 1996). The ISO spectrum of HD100546 is very similar to that of comet Hale-Bopp (Malfait et al. 1998). These systems are thought to have a population of sun-grazing comets, in order to explain transient gaseous emission features seen in their spectra (e.g. Grady et al. 1997). However, crystalline silicates are not seen in the spectra of most young stellar objects (e.g. Hanner et al. 1998a). Moreover, they are not present in spectra of the diffuse ISM or molecular clouds, such as the Trapezium. Grain destruction in the ISM is an efficient process. Thus, if the comet grains formed in circumstellar outflows, one must explain how they survived destruction in the ISM and why they are not apparent in spectra of the ISM or YSOs.

Thus, the origin of the crystalline cometary silicates remains puzzling. If they formed in the inner solar nebula, then their presence in comets requires significant mixing in the solar nebula. If they are circumstellar in origin, one has to explain why their spectral features are not visible in interstellar dust. The signatures of crystalline silicates appear in the spectra of young stellar objects only at a late evolutionary stage, when comets are the likely source of the dust.

Acknowledgements

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